

Microstructural changes in aged vapour-quenched Mo-Au alloys

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Thin films of single-phased alloys of the normally immiscible metals, molybdenum and gold, have been prepared by vapour co-deposition onto cool substrates. The microstructural changes induced by heating were studied by electron diffraction and electron microscopy which revealed that the alloys decomposed into a two-phase aggregate of molybdenum and gold by precipitation both within the films and on the free surfaces. Eventually the gold was entirely removed from the specimens. Electrical resistance measurements indicated that the decomposition process obeyed second order kinetics and was associated with an activation energy that increased as the transformation proceeded.

1. Introduction

It is well known that by condensing vapours on cold substrates (vapour-quenching), metastable phases, that are unattainable by conventional techniques, can be produced in metals and alloys. A review of much of the work concerning this phenomenon has been given by Chopra [1]. In particular, because a solid sample can be made in a manner that minimizes or precludes diffusion, it is possible to prepare metastable binary solid solutions with solute contents considerably enhanced over those normally possible. This has been achieved for metals of the same structures, metals of dissimilar structures and metals of negligible mutual solubility [2-5]. Depending upon specific conditions, such alloys can be initially amorphous or crystalline and can be transformed into two-phased aggregates. The properties and behaviour of such abnormal manifestations of alloys are of intrinsic interest and also of interest from the aspect of possible applications. Furthermore the ability to increase the solute content to levels corresponding to extremely high supersaturation ratios, at any temperature, provides a possible means of obtaining large densities of second phase particles by precipitation.

Presented herein are the results of an investigation into the structure of vapour-quenched molybdenum-gold alloys and the changes wrought by subsequent heat-treatments. This system was chosen primarily because the elements exhibit very small mutual solubilities

[6] and apparently form no intermediate phases, which provides an example of an extreme situation in which even dilute solutions would be highly supersaturated. Some attention was paid to molybdenum, itself, to establish conditions under which single-phased alloys could be prepared without possible complications from unusual crystalline modifications that can be exhibited by molybdenum and other metals [1, 7].

2. Preparation of the specimens

Films of molybdenum and of the alloys were obtained by condensing unary or binary metallic vapour beams upon suitable substrates. Some molybdenum films were made within an unbaked bell-jar in which the vacuum was in the range of 10^{-5} to 10^{-4} Torr. The remainder of the molybdenum samples and all of the alloys were fabricated within an apparatus in which vacua of 10^{-8} Torr and better were obtained and, apart from an initial transient rise to a few times 10^{-7} Torr, generally could be maintained during the preparation of the sample. Molybdenum and gold were vapourized from separate, independently controllable sources that were heated electrically. The measurement and control of the vapour fluxes was made possible by continuously observing the change in the resonant frequency of a quartz crystal [8, 9] using electrical circuitry designed by Dryer [10] while a system of magnetically movable shutters provided control over the periods during which the crystal and

substrates were exposed. The substrates were positioned adjacent to the crystal and were held within a stainless-steel mount which could be cooled by liquid nitrogen or heated electrically to a few hundred degrees centigrade.

The films were condensed either upon cleaved crystals of rock-salt, from which they were easily stripped for examination, or upon 3.5 mm by 20 mm quartz strips previously equipped with appropriate electrodes to facilitate the measurement of electrical conductivity. In each experiment substrates of both types were mounted within the chamber so that subsequent microstructural and electrical observations would relate to samples prepared under the same conditions. Deposition rates were not high and films of 300 to 600 Å thickness were produced in times typically of the order of an hour. The substrate temperature rose initially during the deposition period so that most samples were mainly formed at temperatures between 150 and 200°C. Under these conditions the initial objectives of the investigation were satisfactorily attained.

3. Heat-treatments and examination

After preparation the samples were heat-treated in several ways while the changes in electrical resistance were monitored and the corresponding microstructural modifications subsequently examined by electron microscopy. In a few cases, relatively low-temperature anneals were conducted prior to the removal of the specimens from the condensation apparatus. Also, a number of foils were heated upon a hot-stage within the electron microscope. However, most treatments were conducted in an electrically-heated quartz tube-furnace containing flowing dry hydrogen. The types of heat-treatments used were: isothermal ageing; cycles of constant heating and cooling rates; and isothermal anneals in which the temperature was changed from one value to another to enable estimates to be made of the activation energies of the processes taking place.

4. Results

4.1. Molybdenum films

Those films prepared in low vacua were condensed nominally at room temperature, but the true temperatures were indubitably greater because of radiant heating by the molybdenum filament. Deposition rates in these cases were rather greater than within the special chamber so

that films up to 1000 Å were made in 30 min. The samples were very fragile and fragmented easily when stripped from the sodium-chloride substrate. For this reason a number were backed with a thin layer of carbon to augment their strength.

In all cases the samples were extremely fine-grained with crystallite diameters less than 50 Å. The electron diffraction patterns were correspondingly diffuse, sometimes sufficiently so to warrant the adjective amorphous. In others the diffraction patterns corresponded to an fcc structure; none were bcc. When heated within the microscope, those samples that had been backed with carbon yielded little information because of the interfering effects of carbide formation. Even for the carbon-free samples the observations were usually impeded, and prolonged study above 300°C precluded, because the poor vacuum within the microscope allowed oxidation of the molybdenum, especially within the areas illuminated by the electron beam. However, the observations showed that the amorphous structure was replaced by the fcc structure but that the latter was relatively stable. For example, exposure to 480°C in a heat-treatment for which the sample was above 400°C for over 1 h produced no structural change in the fcc film.

These results are generally similar to those that have been reported [11, 12] for films made by sputtering in argon or condensation within an electron microscope. In improved vacua the maximum temperatures of the substrates on which molybdenum can be condensed in the amorphous or fcc modification can be lowered. Condensation on substrates cooled by liquid helium [13] in residual pressures of 10^{-10} Torr results in an amorphous film that, upon heating, transforms to fcc molybdenum around 60 K and then to the normal bcc structure at 310 K. When the substrates were cooled by liquid nitrogen, the fcc structure formed initially. It is clear that the temperatures at which the fcc modification is formed and also the temperatures to which it can subsequently be heated without transformation are profoundly influenced by the quality of the vacuum in which the molybdenum vapour is condensed. The observations demonstrate that as well as being desirable in order to minimize the incorporation of impurities into the films, a low background pressure is a prerequisite for the production of bcc structures at temperatures that are low enough to avoid simultaneous phase

separation when condensing the binary vapour beams. Molybdenum films condensed in a vacuum several orders of magnitude better than that in the bell-jar were invariably bcc. Complications that might have been caused by the production of an fcc modification were thus avoided. A further benefit that probably resulted from the increased purity of the films was a considerable improvement in their mechanical stability compared to these prepared in the bell jar.

These molybdenum films, when annealed in hydrogen, showed little observable change in times of a few hours below 450°C. At higher temperatures grain growth occurred and grains over 1000 Å across could be obtained by exposure to high temperatures. Figs. 1 and 2 demonstrate the change in grain size after ½ h at 900°C.

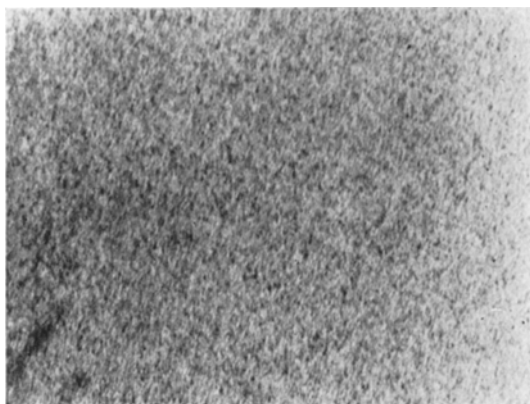


Figure 1 Electron transmission micrograph of vapour-quenched Mo. × 60 000.

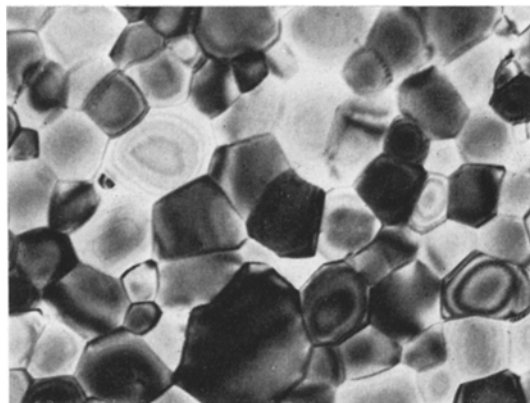


Figure 2 Electron transmission micrograph of vapour-quenched Mo, annealed ½ h at 900°C. × 55 000.

occasions this was effected by the superposition of a standard, either aluminium or thallium chloride, upon the sample. These experiments demonstrated that the bcc rings were invariably spaced in accord with a lattice parameter within ¾% of that of bulk molybdenum so that for data obtained in the absence of an incorporated standard, the molybdenum pattern was used as a means of analysing the fcc rings. The values obtained showed no significant dependence upon the temperature at which ageing was performed and, as shown in Table I, they were consistent with that of bulk gold although in all cases somewhat lower than it. Whereas the values reported here were not obtained with high precision, the magnitudes of the discrepancy with the bulk gold parameter coupled with the fact that all values were on the low side suggests

4.2. Alloy films

Alloys containing from 2 to 30% Au and also 60% Au were prepared. In all cases the samples were single-phased structures; those that were rich in molybdenum were bcc while the 60% Au composition was fcc. For each case it was possible to induce a transformation from a single to a two-phased structure by a suitable heat-treatment. When the initial phase was bcc the transformation involved the formation of an fcc phase and vice-versa as was revealed by the development of duplex electron diffraction patterns. A number of the patterns for specimens in which the duplex structure was strongly developed were analysed to determine the lattice parameters of the relevant phase. On several

TABLE I Lattice parameters of the fcc phase

	Alloy			
	Mo-10 Au	Mo-30 Au	Mo-60 Au	Bulk gold
Lattice parameter	3.92	4.02	4.05	
	3.94	4.02	4.09	
	3.96	3.95	4.03	
	4.0	3.99	4.06	
		4.02	4.03	
			4.07	
			4.05	
			4.03	
		4.00		
		3.99		
Mean	3.96	4.0	4.04	4.0788 [25]

that the lattice parameter of the gold phase is truly less than its bulk value. This might be due to retained molybdenum, which has an atomic size that is smaller than that of gold although lattice parameters reduced by up to 0.3 to 0.4% have been reported for small gold crystals [14] and thin plates [15].

For all molybdenum-rich alloys, continued annealing, after the production of the duplex diffraction pattern, caused a gradual diminution in the intensity of the fcc contribution and its eventual disappearance. As the most extensive studies were conducted upon alloys near the 30% Au composition the behaviour of these will be described first.

The response to various conditions of heat-treatment can be divided into three parts and is illustrated in Fig. 3 in which the combinations of

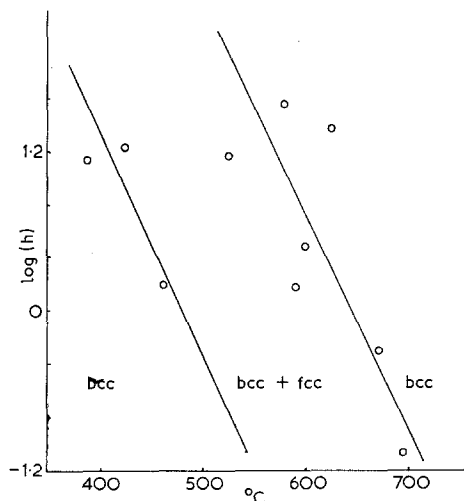


Figure 3 Annealing time versus temperature plot depicting nature of the resulting diffraction pattern.

time and temperature are divided into three regions. Plotted on the diagram are points selected to illustrate the consequences of conditions near the boundaries that separate the regions. In the first regime fall those combinations of time and temperature for which no change was discernible in the selected-area diffraction patterns. In the central portion are those combinations that yielded a duplex diffraction pattern while the third region depicts conditions for which no fcc reflections were visible on the screen of the microscope. The general behaviour was such that a path passing from region one through region two into region

three was associated with the appearance of the fcc rings which increased in intensity, reached a maximum, and thereafter declined until no longer detectable. The rate at which the process was accomplished was temperature-dependent and became so rapid above 800°C that the duplex diffraction pattern was not observed. Examples of the diffraction patterns for selected heat treatments are presented in Figs. 4 and 5.

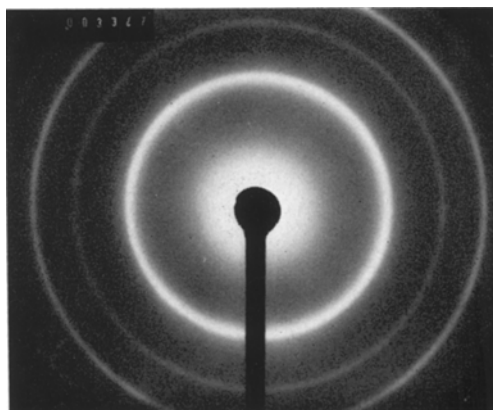


Figure 4 Electron diffraction pattern of vapour-quenched Mo-30 Au; bcc.

Those annealing conditions that caused decomposition of the alloys also produced a gradual increase in grain size. However the crystallites were generally still too small when the duplex diffraction patterns had developed most strongly to permit the detection of gold particles by bright-field microscopy. At somewhat larger grain sizes, although the fcc

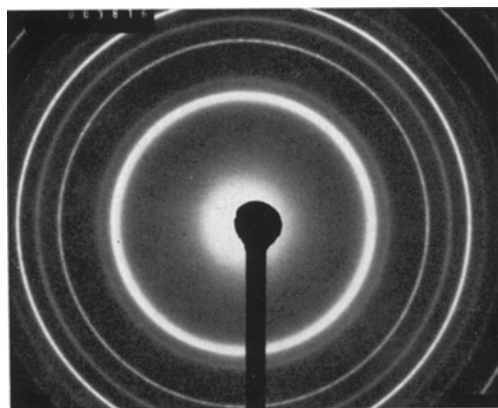


Figure 5 Electron diffraction pattern of Mo-30 Au after 15 h at 525°C; bcc + fcc.

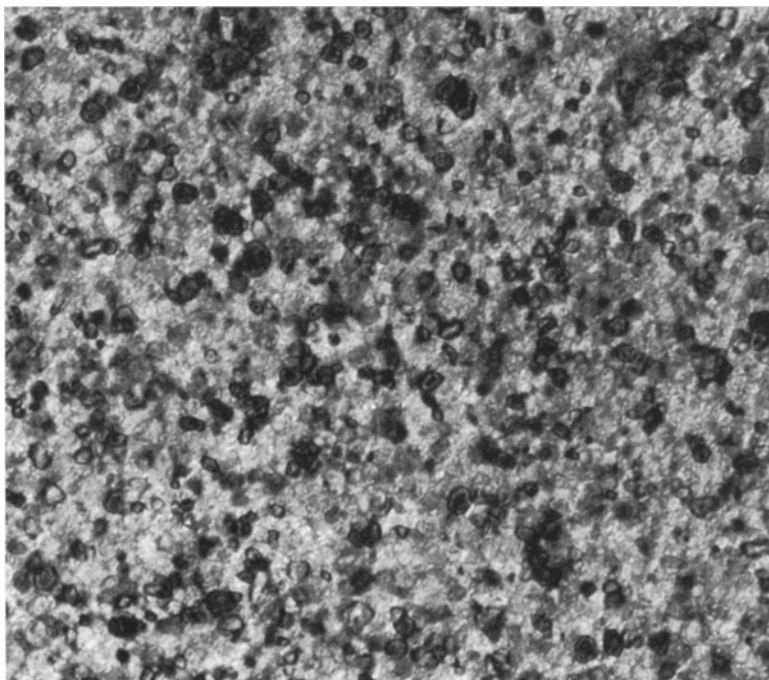


Figure 6 Electron transmission micrograph of Mo-30 Au after 3 h at 600°C. $\times 66\ 000$.

contribution to the diffraction patterns had by then become fainter, a fine distribution of particles was visible (Fig. 6). The nature of all the particles was not established; they were probably gold because some could often be identified by operating the microscope in the dark field mode with the aperture positioned to accept a segment of an Au diffraction ring. By annealing at elevated temperatures it was possible to obtain grains of the order of 1000 Å in which there was little evidence of the presence of gold.

The general behaviour described above was found for all the molybdenum-rich alloys examined. However, one series of 10% Au alloys was prepared with an initial grain-size of approximately 300 Å because of a rise in the substrate temperature to 250°C. The larger grain size in the as-prepared samples reduced the obscurity, in the early stages of the decomposition, caused by the very fine grain size of the other samples. Selected-area diffraction patterns of these samples were in most cases bcc but from a few areas, very faint fcc contributions were detectable. It is apparent, then, that these preparation conditions are near the upper limit of those that enable the formation of an entirely

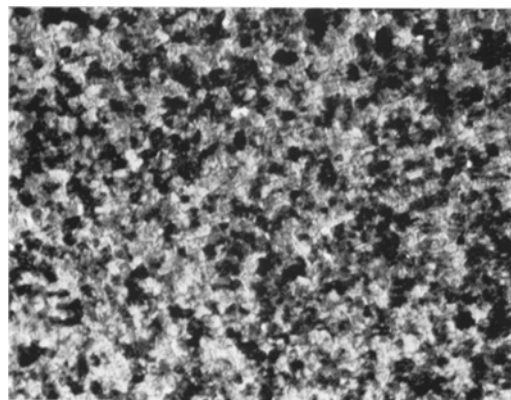


Figure 7 Electron transmission micrograph of Mo-10 Au as-quenched. $\times 66\ 000$.

single-phased specimen. Under bright-field conditions, as indicated in Fig. 7, the grains were somewhat blurred inside, possibly from the combined effects of overlapping grain boundaries, imperfections and solute inhomogeneities. When the films were annealed between 500°C and 600°C, the clarity of the images improved, and even when negligible changes in the grain

size were observed, a clearly visible distribution of gold particles developed (Figs. 8 and 9) which gave rise to a strong fcc contribution to the diffraction patterns and were also visible in dark field conditions.

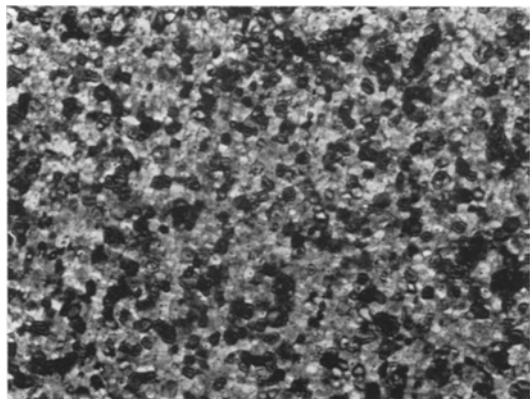


Figure 8 Electron transmission micrograph of Mo-10 Au after 3 h at 600°C. $\times 66\ 000$.

In general, no definite conclusions can be drawn with respect to the morphology of the gold phase in those cases when the grain size remained very fine. For the combinations of conditions that yielded micrographs such as Fig. 6 on which a dense distribution of well-defined particles can be seen, it seems reasonable to conclude that precipitation occurred within the alloy. At higher temperatures this microstructure was not observed; instead, changes occurred

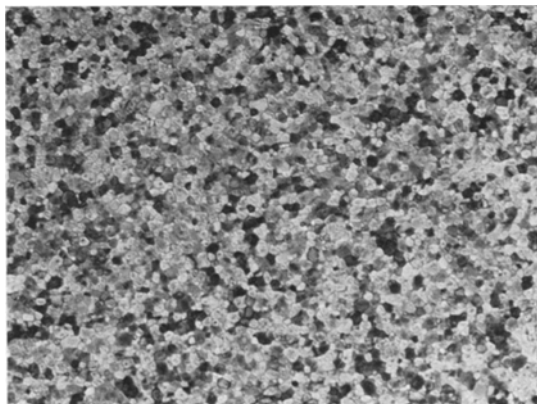


Figure 9 Electron transmission micrograph of Mo-10 Au after 3 h at 600°C. $\times 66\ 000$.

rapidly to yield micrographs of the type shown in Figs. 10 and 11. Distributed over these are dark spots of poor definition and low contrast which suggests that they might arise from particles of gold formed upon free surfaces. Besides these, as is particularly evident for the more concentrated alloys, is a form of regular modulated contrast that is frequently similar to that of moiré fringes, and offers further evidence for the presence of a gold layer upon the free surface. At even higher temperatures relatively large grains are attained in which little evidence of any gold can be found.

In contrast to the molybdenum-rich composition, alloys of 60% AuMo appeared to evolve into a similarly sized aggregate of Mo and Au grains. These alloys were not subjected to extensive study but in this case, also, there was a tendency for the Au diffraction rings to diminish in intensity when the samples were exposed to elevated temperatures.

4.3. Electrical resistance measurements

The electrical resistance of all films, measured from -100 to 250°C within the preparation chamber, showed no irreversible changes. When exposed to air their resistances increased by approximately 5% mostly during the first 30 min of exposure. Such increases have been reported for a variety of films [16] and are presumably associated with adsorbed gases or possibly a thin oxide layer. Whatever the agency responsible for the increase it is removed from molybdenum films between 300 and 400°C in hydrogen at a heating rate of 200°C h^{-1} as shown by the change in rate of resistance increase in Fig. 12. Except for this effect no significant irreversible changes occur in the resistance of the molybdenum samples below 450°C . As can be seen from Fig. 13, irreversible reductions in the resistance of Mo-30 Au alloys begin near 300°C . The precise reason for this, in comparison with the case of molybdenum, cannot be decided from the microstructural observations, although it is entirely reasonable to expect the alloy to be less perfect initially than the pure element.

The resistance variations depicted in Figs. 12 and 13 are typical of the general behaviour. However, the actual numerical values of the resistivities of the as-prepared films varied from 50 to $110\ \mu\Omega\ \text{cm}$, irrespective of composition. Those results shown were obtained from a Mo film $35\ \text{nm}$ thick with an initial resistivity of $87 \times 10^{-6}\ \Omega\text{cm}$ and a Mo-30 Au Alloy, $27\ \text{nm}$

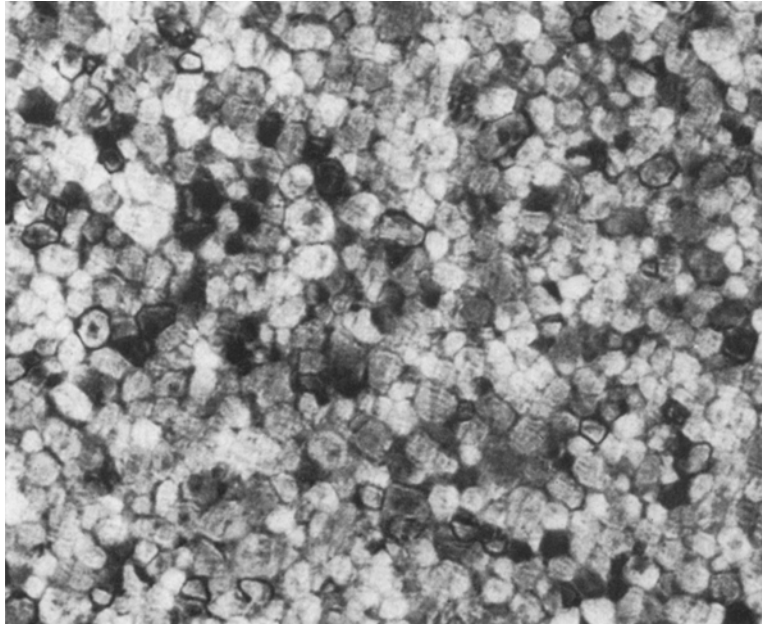


Figure 10 Mo-30 Au after 5 min at 690°C. $\times 125\ 000$.

thick with an initial resistivity of 83×10^{-6} Ωcm .

An interesting observation is included on Fig. 13 in the form of dotted lines which show the results of interrupting the rising temperature by successive cooling and heating stages. It can be seen that as ageing proceeds the temperature coefficient of resistivity corresponding to these stages gradually increased. For some bulk samples of substitutional alloys the temperature coefficient of resistivity decreases with increasing

solute contents [17]. Some pure metal films in the amorphous condition show little or no variation in resistance with temperature [1]. In the present case the behaviour parallels the

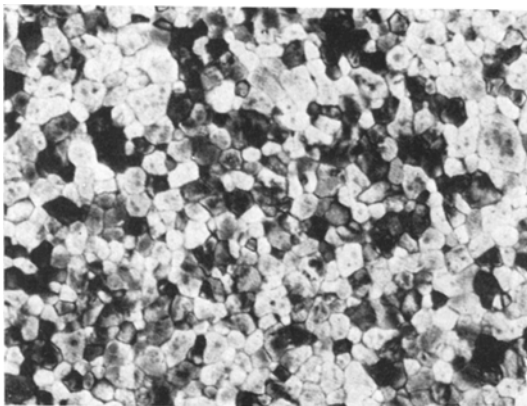


Figure 11 Mo-10 Au after 5 min at 690°C. $\times 125\ 000$.

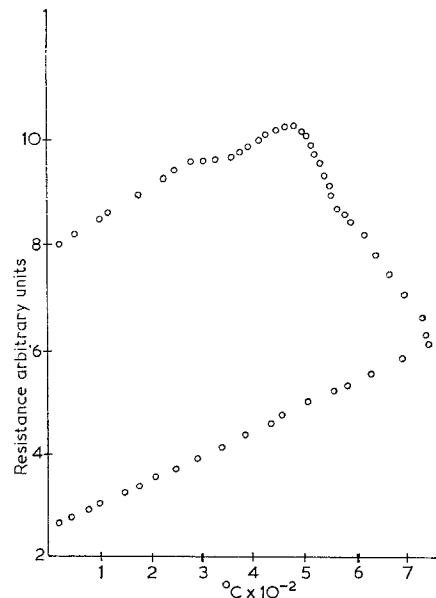


Figure 12 Resistance versus temperature plot for a heating rate of $200^{\circ}\text{C h}^{-1}$; Mo.

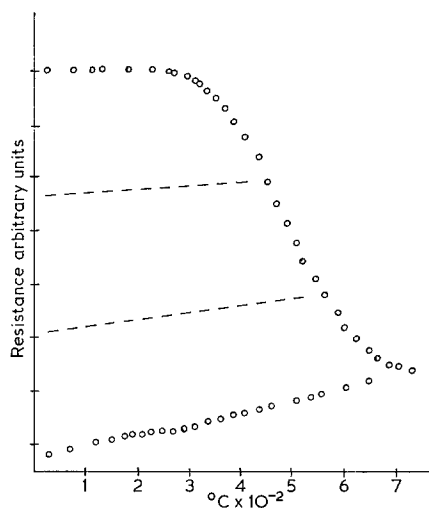


Figure 13 Resistance versus temperature plot for a heating rate of $200^{\circ}\text{C h}^{-1}$; Mo-30 Au.

increasing perfection of the films and the reduction in the gold content.

Estimates of the activation energies obtained by changing the temperature during isothermal ageing are presented in Table II. Because of the

TABLE II Estimated activation energies for the process reducing the electrical resistance

Temperature change ($^{\circ}\text{C}$)	Activation energy (kcal mol $^{-1}$)
<i>Mo-30 Au</i>	
397-480	31
	28
480-556	43.5
	41
549-582	39
	35
640-741	43
470-508	23
508-561	45.6
561-575	44.5
<i>Pure Mo</i>	
640-750	59

large temperature changes used in these experiments the numbers quoted are subject to considerable errors. However it can be seen that the activation energies ranged from 20 to 50 kcal mol $^{-1}$, with some indication for the Mo-30 Au alloys that the relevant value increased as the

transformation progressed. This is consistent with the exhaustion of the easiest processes during a complex reaction.

The isothermal anneals confirmed the behaviour in the cyclic treatments in that appreciable reductions in the resistances of the alloys took place at temperatures that induced no microstructural modifications that could be detected microscopically. These heat-treatments were generally of short duration but a sample of Mo-30 Au was held at 580°C for 7 h during which its resistance changes obeyed, quite closely, second order kinetics. In Fig. 14 the

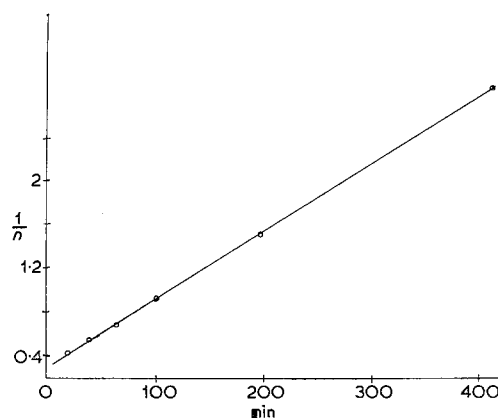


Figure 14 Graph of the reciprocal of the excess resistance against time at 580°C ; Mo-30 Au.

reciprocal of the excess resistance, $1/n$, is plotted against the time, t . The straight line indicates that the behaviour is described by the equation $-dn/dt = (\text{constant})n^2$ even though several processes were presumably occurring.

5. Discussion

These observations demonstrate that single-phased mixtures of Mo and Au, which possess extremely limited mutual solubilities, can be prepared by physical co-deposition upon substrates maintained below 200°C in vacua of better than 10^{-7} Torr. They also suggest that the structure adopted by the alloy is that of the component present in the greater quantity. Support for this statement was obtained from samples in which the composition varied from Au at one end to 30% Au in Mo at the other and across which the diffraction pattern changed from fcc to bcc. Furthermore, no evidence was found to suggest that intermediate phases were formed during the decomposition of the alloys

which confirms the fact that the phase diagram of the binary system Mo-Au is a simple eutectic [6].

Ageing in hydrogen above 390°C can lead to the decomposition of single-phased mixtures of Mo and Au, rich in molybdenum, into an aggregate of molybdenum grains and gold particles and that continued ageing, particularly at higher temperatures results in the eventual loss of the gold. The last characteristic not only curtailed the range of heat-treatments over which the phase separation could be studied but also precluded subsequent morphological developments of the two phase aggregates. Moreover, because the fcc rings gradually decayed in intensity rather than undergoing changes consistent with a process culminating in a few large particles, it is likely that the gold was lost by evaporation. For this to be so the gold would need to partition to the free surface of the foil, and the role played by such a process in the overall decomposition becomes an interesting question.

It is generally true [18] that when an extant phase is not representative of the equilibrium state, the transformation to equilibrium can occur by several mechanistic paths of which one might dominate or two or more might operate simultaneously, depending upon the conditions. Particles of a stable phase formed by continuous precipitation reactions in large samples of substitutional solid solutions, usually occur at heterogeneous sites such as grain boundaries, unless they are structurally related to the matrix in such a way that small particles can form coherently and then homogeneous precipitation can take place as in Ni-Al [19] and Cu-Co [20] alloys. According to classical nucleation theory [21], increasing the supersaturation by reducing the reaction temperature can, in principle, help the homogeneous nucleation of incoherent nuclei; however the formation of the incoherent interface remains a difficult process mechanistically and as the temperature is reduced the transformation can be suppressed entirely or replaced by the precipitation of metastable phases. An extreme example of such an event is the formation of Guinier-Preston zones in a variety of alloys. The present case is one of a substitutional solid solution that is extremely super-saturated at any temperature at which it is solid and for which the equilibrium phases differ greatly in nature. However, the samples studied here were 250 to 500 Å thick. This has the consequence that the free surfaces of the specimens can assume importance as hetero-

geneous precipitation sites, as occurs for example when thin foils of Al-Zn alloys are aged within the electron microscope [22]. Furthermore, because the thin samples permitted the loss of gold, the effects of the combination of high super-saturation and high homologous temperatures, which is not normally possible for precipitation from solid solution, could not be studied.

It is clear that the decomposition of the foils entails a competition between processes of internal phase separation and those associated with the migration of the gold to the surface, where an additional competition is to be expected between the removal of the gold from the surface and the nucleation and growth of gold particles from the ad-atom population thereon. Superimposed upon and interacting with these processes is grain growth within the sample. The consequences of these competing processes can be expected to be temperature dependent and the overall transformation to be of considerable complexity. For samples that retained a very fine grain size, little can be definitely concluded about the microstructural changes that gave rise to the gold diffraction pattern. It is, however, worth noting that a large volume fraction of such samples constituted the grain boundaries so that the copious grain-boundary area was available to promote heterogeneous precipitation. Indeed, a monolayer segregate could account for most of the gold content. At larger grain sizes the evidence points towards precipitation within the foils and upon their surfaces.

On the basis of the foregoing observations a tentative description of the broad characteristics of the transformation of these alloys can be advanced. As the temperature is increased, atomic mobility becomes sufficient to permit localized phase separation within the matrix either within the crystallites or at boundaries which subsequently migrate away. The result is a very finely dispersed, two-phase aggregate. At the same time a tendency for gold migration to the free surfaces, presumably by grain-boundary diffusion, develops. With increasing temperature the latter process becomes more rapid and, with the aid of the boundaries sweeping through the matrix, is eventually capable of essentially draining the interior of solute. As the population of gold atoms develops on the free surface some will desorb to the vapour phase while others can be expected to participate in the nucleation and

growth of gold particles in the manner that can occur in heterogeneous nucleation from the vapour phase. [23, 24]. After sufficient time, less than $\frac{1}{2}$ h at 900°C, the gold surface population is desorbed entirely.

The gradual variation in the evolution of the decomposition processes envisaged above is consistent with the tendency for the apparent activation energy to increase as the reaction progressed and also with the fact that the decrease of resistance, at the constant heating rate used here, occurred continuously rather than in separable stages.

It is to be expected that the influence of the free surface would be diminished and the role of internal phase separation accentuated by increasing the film thicknesses. In the present work the actual thicknesses of the specimens were dictated by the controllable lifetimes of the molybdenum filaments. These, as a consequence of being used near the melting point of molybdenum, were prone to develop hot spots which not only gave rise to flux-rates that were difficult to control but also led to filament-failure. Consequently, attempts to prepare thick films in any one process were unsuccessful.

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